IN-SITU REMOVAL OF ARSENIC FROM GROUNDWATERS BY USING PERMEABLE REACTIVE BARRIERS OF ORGANIC MATTER/LIMESTONE MIXTURES.

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Abstract: In this study, two different mixtures of municipal compost, limestone and zero-valent iron were assessed in two column experiments on acid rock treatment. The effluent solution was systematically analysed throughout the experiments and precipitates from both columns were withdrawn for scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffractometry were analyzed. Results showed that waters were cleaned of metals, arsenic and acidity, but chemical and morphology analyses suggest that metal removal was not due predominantly to biogenic sulphide generation, unless simple organic carbon compounds were supplemented. Instead, metal removal can be attributed to pH increase, i.e. metal (oxy)hydroxides and carbonates precipitation and sorption onto organic matter could also contribute to metal removal to some extent. Arsenic removal was typically associated to co-precipitation and/or adsorption with iron and aluminium (oxy)hydroxides. When zero-valent iron was present, cementation of copper also occurred.

Key words: acid mine drainage, passive remediation, permeable reactive barrier, sulphate-reducing bacteria, arsenic removal.

INTRODUCTION
Acid rock drainage (ARD) is one of the most serious environmental concerns associated with the mining industry around the world. It is generated by oxidation of pyrite and other metal-sulphide minerals in rock wastes and tailing impoundments. Metal-sulphides other than pyrite may release Zn, Cu, Cd, As, Ni, Pb,... ARD is thus characterised by high acidity (pH<3) and a high concentration of sulphates (up to 5000
mg dm$^{-3}$) and metals (Fe, Zn, Pb, Cd, Cu, …) and non-metals (As, Se, Sb). This acidic-, metal-contaminated water adversely impacts on both surface and ground water, with the result that treatment is necessary to meet legislation standards. Current techniques for ARD treatment consist of ex-situ chemical treatment, which conventionally involves the addition of an alkaline agent or sulphide in order to promote metal precipitation as hydroxides or sulphides. An alternative approach is metal precipitation by bacterially in-situ generated sulphides. This biological approach seeks to induce sulphate reduction by means of sulphate-reducing bacteria (SRB), which under favourable conditions convert sulphate to sulphide by the oxidation of organic carbon. Sulphate-reduction reactions consume $\text{SO}_4^{2-}$, produce $\text{H}_2\text{S}$ and result in an increase in alkalinity and pH. Toxic metal (M) removal from the solution occurs via formation of metal sulphide precipitates (MS(s)).

ARD in-situ bioremediation has in last decades attracted the attention of biotechnologists. The most recent application is the permeable reactive barrier (PRB).$^{5,6}$ A PRB consists of digging a trench in the aquifer and fill it with an appropriate reactive material able to induce physico-chemical and/or biological processes that remediate contaminated groundwater. This treatment is passive so that once installed low maintenance is required.

PRB materials for AMD bioremediation include a SRB source (typically an environmental organic sample such a lake sediment) and an organic substrate to promote and maintain bacterial activity. Additional proposed materials are limestone (to neutralise pH and facilitate bacterial activity),$^2$ iron (to induce reducing conditions and hydrogen generation, which appears to be a helpful electron donor for SRB)$^3$ and silica sand or gravel (to enhance permeability).$^4$

The present paper summarizes the potential use of a municipal compost as a widely available organic mixture for use in in-situ permeable reactive barriers. This work forms part of the research on the mine accident at the Aznalcóllar Mine (Spain), which took place in 1998, when a tailing pond was breached. As a result $4\times10^9$ m$^3$ sludge and $2\times10^6$ m$^3$ acidic drainage flooded over the River Agrio valley. Although most of it was subsequently removed, pollution remaining in the soil resulted in acidic, metal and arsenic contaminated leachates draining into the groundwater. The installation of a PRB was postulated as a solution.

The main aim objectives of this work was to ascertain whether a municipal compost (accompanied by calcite and optionally by iron) could remediate a metal and arsenic containing acid water and could thus be a potential material for PRB under these high water flux conditions.

**EXPERIMENTAL**

**Experimental Methodology**

Two reactive mixtures were assessed in column experiments (i.d.=2.5cm, l=20cm). Compositions (in vol %) are given in Table 1. Column 2 contained 5 vol % zero-valent iron aggregates to promote reducing conditions. Creek sediment acted as the SRB source, municipal compost was the provider of the carbon source and limestone was used as the neutralising agent. Compost was provided by Aplicaciones de la Biomasa S.A. from Sevilla (Spain), limestone came from a quarry (2-4 mm size) and iron was supplied by Connelly-GPM, Chicago (Illinois)(8-80 mesh).

Chemical composition of the synthetic mine water was based on analysis of contaminated groundwater of the Agrio aquifer, Aznalcóllar, Spain (Table 2). Metals and anions were added to the dissolution as sulphates and after pH was adjusted.
Table 2: Simulated mine-drainage water composition

<table>
<thead>
<tr>
<th>Conc (mg dm⁻³)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄²⁻</td>
<td>960</td>
</tr>
<tr>
<td>Fe (II)</td>
<td>10</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>20</td>
</tr>
<tr>
<td>Al (III)</td>
<td>10</td>
</tr>
<tr>
<td>As (V)</td>
<td>2</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>20</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2: Composition of column reactive mixtures (in vol %)

<table>
<thead>
<tr>
<th></th>
<th>Column 1</th>
<th>Column 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>Vegetal Compost</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>Creek sediment</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Zero valent Fe</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

The inflowing water was kept in a closed reservoir with low oxygen by bubbling nitrogen and was pumped to the columns, from bottom to top, using a peristaltic pump. The inflowing water feed water was pumped to the base of the column at a flux of 0.34 m/day (17 h average residence time). Both experiments were carried out at room temperature (23±2 ºC). The effluent from both columns was sampled and analysed to determine pH, metal, arsenate and sulphate concentrations. At the end of the experiments fractions of precipitate from both columns were retrieved to be visualised using scanning electron microscopy (SEM) and analysed by energy-dispersive X-ray spectroscopy (EDS) and X-ray diffractometry (XRD).

**Water Sampling and Analysis**

All pH and Eh measurements were made routinely in a sealed flow-through cell placed at the exit of the columns. Effluent samples were collected periodically for metal and sulphate analyses. Samples were filtered (0.22 μm) and acidified with concentrated HCl. Zn, Fe, Cu, Cd and As were measured by inductively-coupled plasma mass spectroscopy (ICP-MS) whereas Al was analysed by inductively-coupled plasma atomic emission spectroscopy (ICP- AES). Sulphate was measured by liquid ion chromatography coupled to an electrical conductivity detector.

**Solid Analysis**

On completion of the experiments, precipitates from both columns were sampled at different distances from the inlet and examined by scanning electron microscope (SEM) and analysed by energy-dispersive X-ray spectroscopy (EDS) and by X-ray diffractometry (XRD) to characterise the precipitates.

**RESULTS**

**Materials effectiveness on acid water treatment**

Material effectiveness was indicated by effluent pH and metal and SO₄²⁻ concentrations. Both columns raised pH from 3 to about circumneutral values. Higher pH for column 2 decreased gradually and, after two months, it achieved pH values obtained for column 1.
in the absence of iron. Effluent metal and arsenic concentrations were in both cases below 0.2 mg dm\(^{-3}\) after the first ten days (retention levels >99%) (Figure 1). Al and Cd concentrations were below detection limits (0.010 and 0.005 mg dm\(^{-3}\) respectively) and they remained unchanged throughout the experiment. Despite the significant metal retention, net sulphate consumption was not detectable.

\[\text{Figure 1: Metal and arsenic concentration evolution for columns 1 and 2.}\]

A brown and pale grey precipitate (iron and aluminium (oxy)hydroxides) formed in the inlet port of both columns from the beginning of the experiment. SEM examination of samples from the two columns showed a pervasive layer coating the surface of all the column material. This layer has no recognisable crystals and is made up of Al, Fe, S and O with minor amounts of Zn, Cu and As. The associated EDS mapping showed that these elements were distributed homogeneously. Octahedral crystals of metallic Cu were also observed in column 2. XRD identification of precipitates was not possible owing to their small amount and poor crystallinity.

\[\text{Figure 2: Aggregates of spherulites made up of Fe, Al, O, S and minor amounts of Zn, Cu and As observed in samples from column 2.}\]
Once the experiments were concluded, three solid samples were collected at 5, 10 and 15 cm from the inlet of column 2, digested totally and analysed. As expected, the metal content decreased for all metals with increasing distance from the inflow port. Cu was the element most affected by distance (more than 97% was located at 5 cm from the inlet of the column). Similar trends were observed for the other metals.

**DISCUSSION AND CONCLUSIONS**

Treatment based on the proposed municipal compost achieved part of the objectives of an ARD remediation, i.e. pH neutralisation and metal removal. Limestone was demonstrated to be an efficient neutralising agent. Carbonate dissolution was able to raise influent pH of 3 to around 6.5, within the range of 5 to 9.5, which is suitable for sulphate reducing bacteria. During the first two months pH in column 2 was higher than in column 1 (Figure 3).

This can be attributed to corrosion of zero-valent iron, which reacts under anaerobic conditions consuming acidity and producing H₂ in accordance with the following net reaction:

\[
\text{Fe}^0 + 2 \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2(\text{g})
\]

Higher pH for column 2 decreased gradually and, after two months, it achieved pH values obtained for column 1 in the absence of iron. This pH decrease can be attributed to the precipitation of (oxy)hydroxides, which formed a film on the Fe⁰ surface coating the reaction sites and thus reducing the reactivity of the zero-valent iron. After iron passivation pH was controlled by limestone dissolution in both columns.

As regards the metals, the treatment in both columns removed more than 99% of the initial concentrations of Fe, Zn, Al, Cu, Cd and As. However most of metal removal did not take place owing to biogenically mediated sulphide precipitation since no appreciable sulphate removal was detected.

Mechanisms whereby metal removal took place may be more related to the pH increase. At neutral pH, an amorphous iron (oxy)hydroxide precipitate with crystals constituted by Fe, Al, S and O was formed as a coating layer. This precipitate acted as a strong secondary adsorption phase for metals and arsenic. These results are in part corroborated by the metal sequential extraction analysis carried out for column 2.
whereby Zn, Cu and Cd were found to be present predominantly in the more mobile form (exchangeable and/or carbonate). It can be speculated that metal release in this fraction is attributable to the desorption from the iron (oxy)hydroxide layer rather than from carbonates, which were not observed in SEM analysis. Zn and Cu were also extracted, in a lesser proportion, by the reducible fraction, revealing associations of these metals with Fe and Mn (oxy)hydroxides. A number of other studies have reported Zn to be strongly associated with Fe and Mn (oxy)hydroxides.24,25

Detailed evaluation for the removal of As is shown in Figure 4, where measured values of Column 2, containing zero valent iron, were below the threshold level defined by the WHO over the full extension of the experiment. In case of column 1 (not containing zero valent iron) during the first 40 days of operation values of As where always above 20 ppb, and after day 40 values of As measured were always between 20 and 10 ppb.

**Figure 4:** Arsenic concentration evolution for columns 1 and 2.

Zero valent iron has been proposed as a new sorption medium for removing both arsenate (AsO$_4^{3-}$) and arsenite (AsO$_3^{3-}$) from polluted waters$^{32-33}$. These studies have shown that Fe may potentially used in PRB technologies to remediate (As) in ground water via surface complexation or precipitation. Specific mechanisms of As removal by Fe$^{0}$ are nowadays under evaluation$^{34}$. Both aerobic and anaerobic corrosion can occur to Fe$^{0}$:

- Anaerobic corrosion: $2\text{H}_2\text{O} + \text{Fe}^{0}(s) \leftrightarrow \text{Fe}^{2+} + \text{H}_2(g) + 2 \text{OH}^{-}$
- Aerobic corrosion: $2\text{H}_2\text{O} + \text{Fe}^{0}(s) + \text{O}_2(g) \leftrightarrow 2\text{Fe}^{2+} + 4 \text{OH}^{-}$
- Oxidation of Fe(II): $\text{Fe}^{2+} + 2\text{O}_2(g) + 10\text{H}_2\text{O} \leftrightarrow 4\text{Fe(OH)}_3(s) + 8\text{H}^+$

Common anions in the aqueous solution may influence the effectivness of Fe$^{0}$ barriers for as remediation through formation of the following new mineral phases and competitive surface sorption/coprecipitation by these phases$^{35}$:

- $3\text{Fe}^{2+} + \text{Fe}^{3+} + \text{Cl}^- + 8\text{H}_2\text{O} \leftrightarrow \text{Fe}_4(\text{OH})_8\text{Cl}(s)$ (chloride green rust) + 8H$^+$
- $4\text{Fe}^{2+} + 2\text{Fe}^{3+} + \text{SO}_4^{2-} + 12\text{H}_2\text{O} \leftrightarrow \text{Fe}_6(\text{OH})_{12}\text{SO}_4(s)$ (sulphate green rust) + 12H$^+$
- $4\text{Fe}^{2+} + 2\text{Fe}^{3+} + \text{CO}_3^{2-} + 12\text{H}_2\text{O} \leftrightarrow \text{Fe}_6(\text{OH})_{12}\text{CO}_3(s)$ (carbonate green rust) + 12H$^+$

The iron corrosion products (oxides and green rusts) are most likely the solid phases that host the sorbed As(V) and As(III). Analysis of As(III) and As(V) adsorption complexes in the Fe$^{0}$ corrosion products and synthetic iron oxides (goethite, lepidocrocite, maghemite, magnetite, and hematite) by X-ray absorption spectroscopy indicate both As species form inner-sphere bidentate complexes.
As expected from the negligible net sulphate consumption and SEM observations, metal sulphides were only occasionally observed by SEM. These observations are consistent with sequential extraction analysis, where metal contents in the oxidisable fraction revealing the presence of sulphides were negligible. One exception was Cu, which was present in the sample collected at 5 cm from the inlet port with a content of up to 11% weight. Cu in this fraction was probably associated to organic matter rather than precipitated as sulphides, as suggested by the high stability of copper complexes with organic matter.24,26

Metal ions like Cu, Ni and Cd can also be removed by cementation. In column 2, where zero-valent iron was present, octahedral crystals of reduced Cu were observed, providing evidence that more reducing conditions were achieved.

Metal adsorption onto organic matter could be another removal process, as reported in the literature.30,31 Although this process cannot be completely ruled out, we have not considered it in our interpretation, with the exception of Cu referred above.

It can be concluded that municipal compost assessed under our experimental conditions was too poor a carbon source to support a continuous SRB activity. The short residence time and/or the slow degradability of some municipal compost must be taken into consideration when planning passive systems based on bacterial sulphidogenesis. The efficiency of the material mixture for heavy metal removal is high and measured values measure were below the threshold levels for ground waters. In the case of arsenic is efficiently removed when in the reactive mixture zero valent iron is used. Values below 10 ppb were measured for the column operation life.

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